Fluid Phase Equilibria 430 (2016) 93–100

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Fusion enthalpies of benzoic acid derivatives, aromatic and heteroaromatic carboxylic acids as a tool for estimation of sublimation enthalpies at 298.15 K

Boris N. Solomonov*, Ruslan N. Nagrimanov, Mikhail I. Yagofarov

Department of Physical Chemistry, Kazan Federal University, Kremlevskaya Str. 18, 420008 Kazan, Russia

ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form
8 August 2016
Accepted 11 September 2016
Available online 14 September 2016

Keywords:
Enthalpy of sublimation
Enthalpy of fusion
Benzoic acid derivatives
Naphthoic acids
Heteroaromatic carboxylic acids

ABSTRACT

In this work a method of estimation of sublimation enthalpies of benzoic acid derivatives and aromatic or heteroaromatic carboxylic acids was developed. The method is based on calculation of sublimation enthalpy from fusion enthalpy of studied compound and of benzoic acid at corresponding melting temperatures and sublimation enthalpy of benzoic acid at 298.15 K.

Calculated sublimation enthalpy values of benzoic acid derivatives containing CH_3-, CH_3O-, F-, Cl-, Br-, I-, NO_2- and other substituents, 1- and 2-naphthoic acids and heteroaromatic carboxylic acids (38 compounds in total) were compared with literature data (at 298.15 K) obtained by conventional methods. In most cases, divergence does not exceed 2–3%.

1. Introduction

Determination of phase transition enthalpies is one of the most difficult and actual problems in chemical thermodynamics. Experimental values of vaporization, sublimation and fusion enthalpies are of a great interest for such disciplines as chemistry, physics and ecology. One of these quantities (sublimation enthalpy) may be measured by various conventional methods [1,2]. However, the usage of conventional methods causes a number of problems that affect sublimation enthalpy magnitude [1–3]. It is especially manifested when the measurements are spent with thermally unstable compounds or at elevated temperatures.

Recently, in our laboratory a method for determination of sublimation enthalpy at 298.15 K without transfer of the substance to the gas phase [3–9] was developed. This method is based on well-known relation between sublimation/vaporization enthalpy at 298.15 K on the one hand and solution and solvation enthalpies at 298.15 K on the other hand. We have elaborated various methods of calculation of solvation enthalpies of aromatic and heteroaromatic compounds. These data together with the solution enthalpies (298.15 K) allowed determining the sublimation and vaporization enthalpies of more than 100 compounds [3–9].

An interesting fact about equality of fusion enthalpies at melting temperature and solution enthalpies in benzene at 298.15 K of aromatic and heteroaromatic compounds was discovered in Refs. [10–12]. It was shown that such relation is possible if two conditions are respected.

Firstly, enthalpy of fusion for the studied compound weakly depends on temperature. Secondly, enthalpy of solution of such compound in hypothetical liquid state in benzene at 298.15 K is close to zero. As a result, we obtained relations, which tie vaporization enthalpy of the studied compound and enthalpy of solvation in benzene at 298.15 K as well as sublimation enthalpy at 298.15 K with solvation enthalpy in benzene and fusion enthalpy at melting point. Thus, the approach for calculating the enthalpy of sublimation at 298.15 K from the fusion enthalpy at the melting temperature and the solvation enthalpy was proposed. Solvation enthalpies of investigated compounds were calculated according to an additive scheme [10–12]. This approach was successfully applied for calculation of sublimation enthalpies of more than 100 compounds [10–12].

However, a number of systems with athermal liquid-liquid dissolution at 298.15 K, for which this approach can be used, is limited. Therefore, in this work we proposed a new scheme for evaluation of sublimation enthalpies using fusion enthalpies at

* Corresponding author.
E-mail address: boris.solomonov@kpfu.ru (B.N. Solomonov).

http://dx.doi.org/10.1016/j.fluid.2016.09.016
0378-3812/